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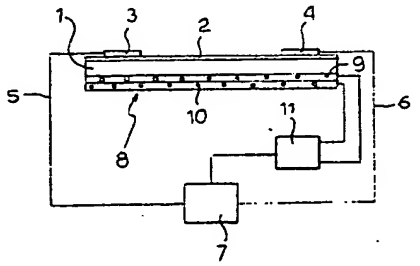
(54) "Gas sensor"

(57) Gas sensor particularly for automotive applications comprising a solid electrolyte (2), normally consisting of β - alumina on which two electrodes (3, 4) are arranged, normally made one of gold and the other of platinum, which are connected to a voltmeter (7) so as to determine, as a function of the measured voltage, the concentration of polluting substances in a gas. The sensor embodies a thermoregulation system (8) to vary selectively and in a controlled way the temperature of the solid electrolyte (2) and correspondingly change the sensor response with respect to pollutants.

Fig. 1



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Description

[0001] The present invention is generally related to sensors for determining the concentration of polluting gaseous mixtures, particularly (though not exclusively) as far as application to exhaust gases of motor vehicle engines is concerned.

[0002] Emission of pollutants produced by these engines and fuel consumption thereof shall both have to be hugely reduced within the next years owing to introduction of more and more strict rules. These objects may be achieved through development of new fuel supply systems and new polluting emission reducing systems.

[0003] A solution to the required rules is represented by the provision of direct injection diesel supply systems, coupled with oxidizer catalytic exhaust apparatuses intended to reduce nitrogen oxides.

[0004] A further adjustment which shall have to be optimized within the frame of motor vehicle internal combustion engines resides in the management of the EGR (Exhaust Gas Recirculation) and of the injection timing, according to a closed loop so has to reduce nitrogen oxides and the particulate, respectively. Moreover use of oxidizer catalysts is also contemplated, which shall have to be operated under the highest efficiency conditions.

[0005] Determining the composition of the exhaust gases and thus the presence and concentration therein of the main polluting components (CO, HC, No_x) constitutes one strategically relevant item in connection with future technologies for emission reduction. For instance in the field of diesel engines measuring the concentration of No_x and HC would enable optimizing operation of $DeNO_x$ catalysts as well as optimized management of the EGR.

[0006] According to the prior art, the only automotive chemical sensors available on the market are the oxyg n sensors of the on/off type (lambda probe) or of the proportional type, both based upon the electro-chemical properties of zirconium oxide (ZrO_2).

[0007] More recently gas sensors for selective measurement of different pollutants have been proposed as industrial prototypes, which are still based on the properties of the zirconium oxide, or upon the electro-chemical properties of other metal oxides, and more particularly of β - Al_2O_3. The latter sensors comprise a solid electrolyte consisting of β - alumina upon which two electrodes are arranged, normally made one of gold and the other of platinum, intended to be exposed to the gas, and measurement means to measure the electromotive force between these two electrodes and to determine, as a function of the measured electromotive force, the concentration of pollutants such as CO, HC, NO_x within the gas.

[0008] Examples of gas sensors of the above-referenced type are disclosed and illustrated, for instance, in GB-A-2.119.933 and FR-B-9207414. The latter document discloses the solid electrolyte undergoing an irreversible treatment by holding it at 600°C for two hours in an atmosphere containing approximately 1% SO_2, so has to improve the sensor response to the presence of carbon monoxide and sulphur dioxide.

[0009] From GB-A-2.119.933 it also known that the response of these β - alumina sensors with respect to the pollutants is variable, in terms of higher or lower sensitivity, as a function of the temperature thereof. It has been discovered that these gas sensors are more sensitive to nitrogen oxides at lower temperatures, while at higher temperatures they are more sensitive to reducing compounds such as HC and CO.

[0010] The object of the present invention is to provide a gas sensor of the type set forth at the beginning which, taking advantage of the above response variability as a function of the temperature, can be conveniently employed in a practical and reliable way, and at relatively low cost, to be directly applied to exhaust apparatuses of motor vehicle engines, so as to optimize operation thereof and reduce pollutant emissions.

[0011] According to the invention, this object is achieved primarily by the fact that a gas sensor of the above-referenced type is provided with a thermoregulation system to vary selectively and a controlled way the temperature of the solid electrolyte.

[0012] The thermoregulation system conveniently comprises heating resistor means and control resistor means, both applied by screen printing onto one face of a ceramic substrate on the opposite face of which β - alumina is deposited also by screen printing.

[0013] The thermoregulation system is normally designed to adjust the sensor temperature between a minimum value of about 300°C, at which the sensor is more sensitive to nitrogen oxides, and a maximum value of about 700°C and up to 900°C, at which the sensor is more sensitive to reducing compounds such as HC and CO.

[0014] The invention will now be disclosed in detail with reference to the accompanying drawings, purely provided by way of non limiting example, in which:

- figure 1 is a diagrammatic representation of one embodiment of a gas sensor according to the invention, and
- figures 2 through 6 are graphs showing the response of the gas sensor according to figure 1 under different operating temperature.

[0015] In accordance with the exemplary embodiment shown in figure 1, a gas sensor according to the invention essentially comprises a ceramic substrate 1 on one face of which a solid electrolyte 2 is applied by screen printing, which is formed by β - alumina for instance produced via "solgel" additioned with silica - alumina glass and sodium oxide, and subsequently thermally processed so has to perform anchoring thereof onto the substrate 1.

A platinum electrode 3 and a gold electrode 4 are arranged in contact with the solid electrolyte 2 and are connected, through respective wires 5, 6, to a measurement instrument 7, for instance a millivoltmeter, provided to measure the electromotive force between the electrodes 3 and 4.

According to the invention, the gas sensor further embodies a thermoregulation system provided to vary the temperature thereof selectively and in a controlled way.

This thermoregulation system, generally designated as 8, includes a heating resistor 9, applied also by screen printing onto the face of the substrate 1 opposite to the solid electrolyte 2, with the interposition of a layer of an inert or electrically insulating material, and a control resistor 9, applied also by screen printing in proximity to the heating resistor 9.

It is important that the heating resistor 9 be electrically insulated relative to the solid electrolyte 2, so has to prevent electrical interferences.

The measurement instrument 7 and the resistors 9, 10 are connected to an electronic control unit 11, through which the heating resistor 9 is supplied with alternate current. The sensitive member of the sensor may be incorporated within a protection body arranged to be fitted in a probe-like fashion for instance into an exhaust apparatus of a motor vehicle combustion engine, so that it is exposed to the exhaust gases. In operation, the voltage measured between the two electrodes 3, 4 by the measurement instrument 7 is indicative of the concentration of the polluting substances (No_x, HC, CO).

[0016] The diagrams shown in figures 2 through 6 depict how the sensitivity and thus the response of the gas sensor with respect to one or the other pollutants varies as a function of the temperature.

Figure 2 shows the response of the sensor at a temperature around 300°C: it can be noticed a high sensitivity with respect to nitrogen oxides, particularly to nitrogen dioxide (NO_2). The signal is negative with respect to the signal corresponding to the environmental air.

Figure 3 shows the response at a temperature around 400°C: the sensor is still remarkably sensitive to nitrogen dioxide and to nitric oxide; in presence of CO (oxidizing) the signal becomes positive.

Figure 4 shows the response at a temperature around 500°C: sensitivity with respect to nitrogen oxides decreases remarkably, while sensitivity to CO increases. The signal in presence both of CO and NO_2 is positive.

Figure 5 shows the response at a temperature around 600°C: sensitivity with respect to nitrogen oxides is still reducing, while sensitivity to CO still increases.

Lastly figure 6 shows the response at a temperature around 700°C: the sensor is practically only sensitive to CO (as well as to HC), while a weak sensitivity to NO_2 still persists.

Accordingly, the thermoregulation system 8 of the gas sensor in accordance to the invention is arranged, by means of the electronic control unit 11, to vary selectively and in a controlled way, during operation, the temperature of the solid electrolyte 2 between a minimum value of about 300°C and a maximum value of about 700°C and more, for instance up to 900°C. In accordance to the above, at the lowermost temperature value the sensor response shall be more efficient and precise with respect to the nitrogen oxides, while at the uppermost temperature value the same result shall be achieved with respect to CO (and HC).

In summary, the gas sensor according to the invention enables to appreciably enhance the measurement precision of the exhaust gases composition of a motor vehicle engine, and thus of the presence and concentration of the main pollutants, which results into a remarkably higher efficiency of the devices provided for reducing these polluting agents (oxidizer catalysts etc) designed to be operatively connected to the sensor. Naturally the details of construction and the embodiments

may be widely varied with respect to what has been disclosed and illustrated, without thereby departing from the scope of the present invention, such as defined in the appended claims.

Thus, while the thermoregulation system disclosed in the case of the shown example is designed to selectively vary the sensor temperature between two utmost values, it is to be pointed out that within the frame of the invention an arrangement may be contemplated according to which the thermoregulation system is arranged to constantly keep the sensor at one of these temperatures. In this case a second almost identical sensor may be provided, whose thermoregulation system shall be designed to constantly keep the temperature thereof at the other value, and possibly even a third identical sensor may be provided whose thermoregulation system shall be designed for instance to constantly keep the temperature thereof at an intermediate value. In alternative a single multi-element sensor may be envisaged, formed by a battery of solid electrolyte sensitive elements arranged onto a common substrate and connected to a single electronic control unit for the electrical supply and for processing the signals provided by the different sensitive elements.

Moreover the solid electrolyte may also consist of alumina in a different crystalline phase, and the related electrodes may also be made of materials which are different than those disclosed in the above.

Lastly the solid electrolyte 2 and related electrodes 3, 4 may also be covered by a porous layer material (ceramic or metallic) providing both a mechanical protection and a chemical filtering function.

Claims

1. Gas sensor comprising a solid electrolyte (2), normally consisting of β - alumina, upon which two electrodes (3, 4) are arranged, normally made one

of gold and the other of platinum, to be exposed to the gas, and measurement means (7) to measure the electromotive force between said two electrodes (3, 4) and determine, as a function of the measured electromotive force, the concentration of pollutants such as CO, HC, NO_x within said gas, the response of said sensor with respect to said pollutants being variable as a function of the temperature, characterized in that it is provided with a thermoregulation system (8) to vary selectively and in a controlled way the temperature of said solid electrolyte (2).

2. Gas sensor according to claim 1, characterized in that said thermoregulation system (8) comprises heating resistor means (8) and control resistor means (10).

3. Gas sensor according to claim 1 or claim 2, characterized in that said thermoregulation system (8) is designed to vary the sensor temperature between a lowermost value around 300°C and uppermost value around 900°C.

4. Gas sensor according to claim 2, characterized in that said solid electrolyte (2) is formed by screen printing onto one face of a ceramic substrate (1), and said heating resistor (9) and said control resistor (10) are applied also by screen printing onto the opposite face of said ceramic substrate (1).

5. Gas sensor according to claim 4, characterized in that said heating resistor (9) is supplied with alternate current.

6. Gas sensor according to claim 2 or claim 4, characterized in that said heating resistor (9) is electrically insulated with respect to said solid electrolyte (2).

7. Gas sensor according to any of the preceding claims, characterized in that the solid electrolyte (2) and related electrodes (3, 4) are covered by a porous material layer having both mechanical protection and chemical filtering functions.

FIG 2

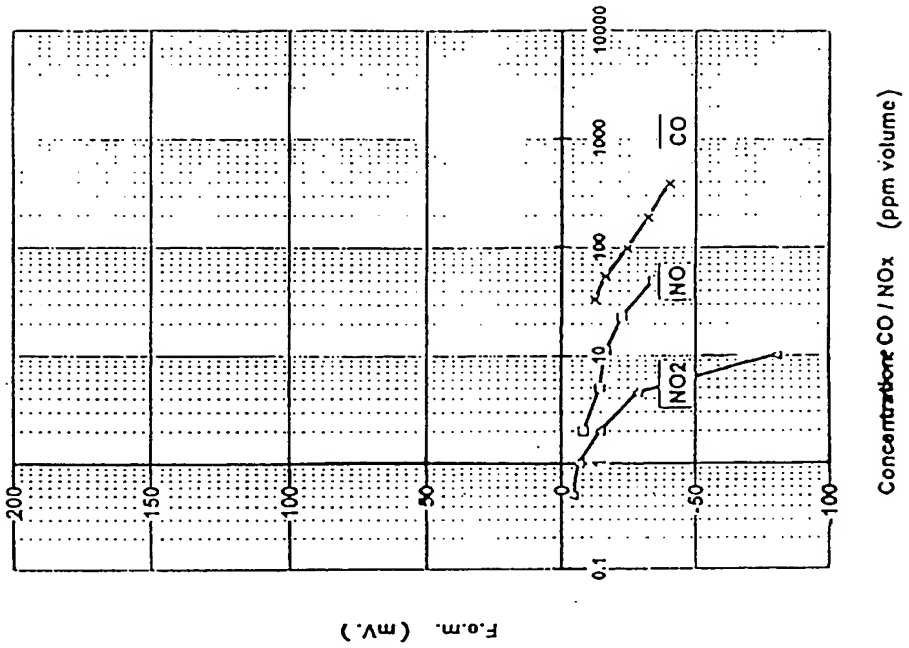

10000
1000
100
10
1
0.1
CO
NO
NO2
200
150
100
50
0
50
100
F.e.m. (mV.)
Concentration CO / NOx (ppm volume)

FIG 1

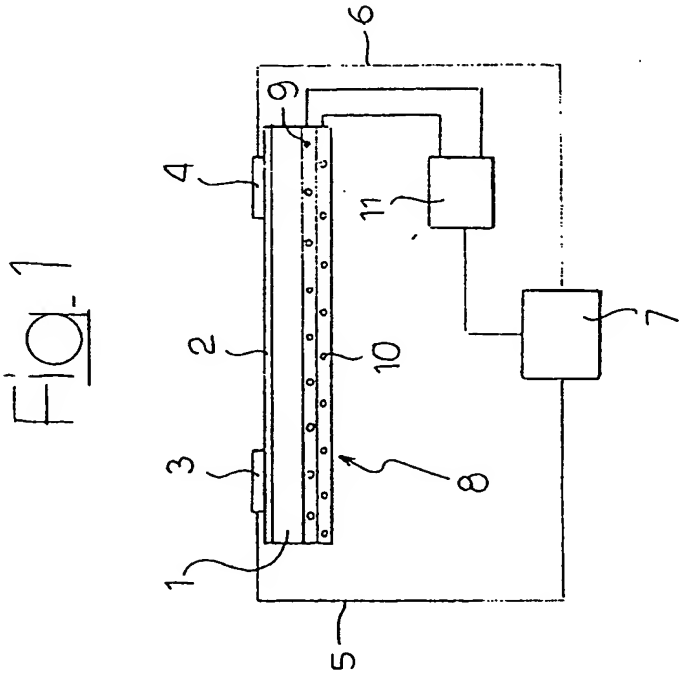

1
2
3
4
5
6
7
8
9
10
11

FIG.4

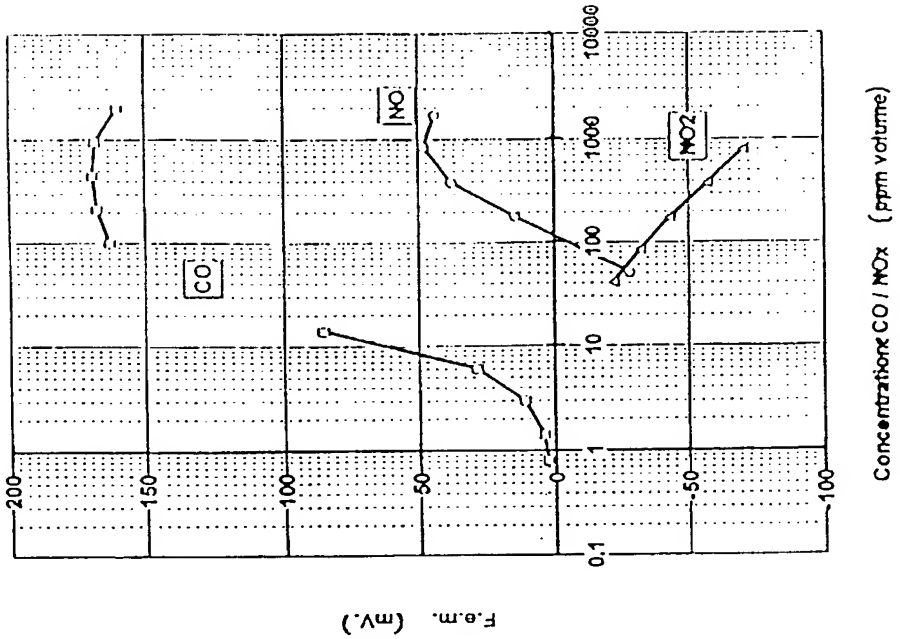
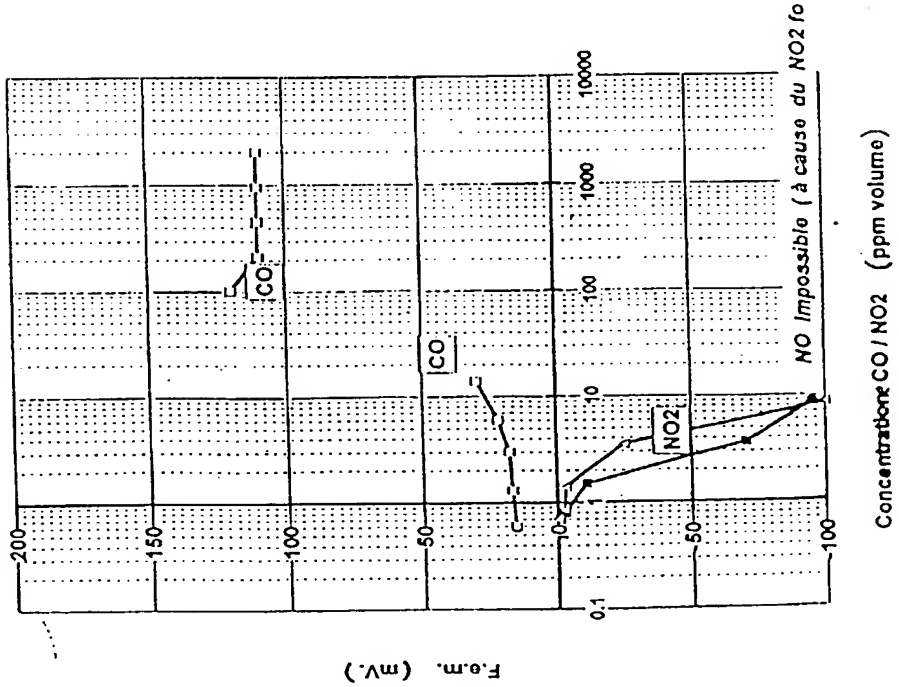

CO
NO
NO2
200
150
100
50
0
0.1
1
10
100
1000
10000
50
100
F.e.m. (mV.)
Concentrations CO / NOx (ppm volume)

FIG.3


CO
CO
NO2
NO impossible (à cause du NO2 fo
200
150
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0.1
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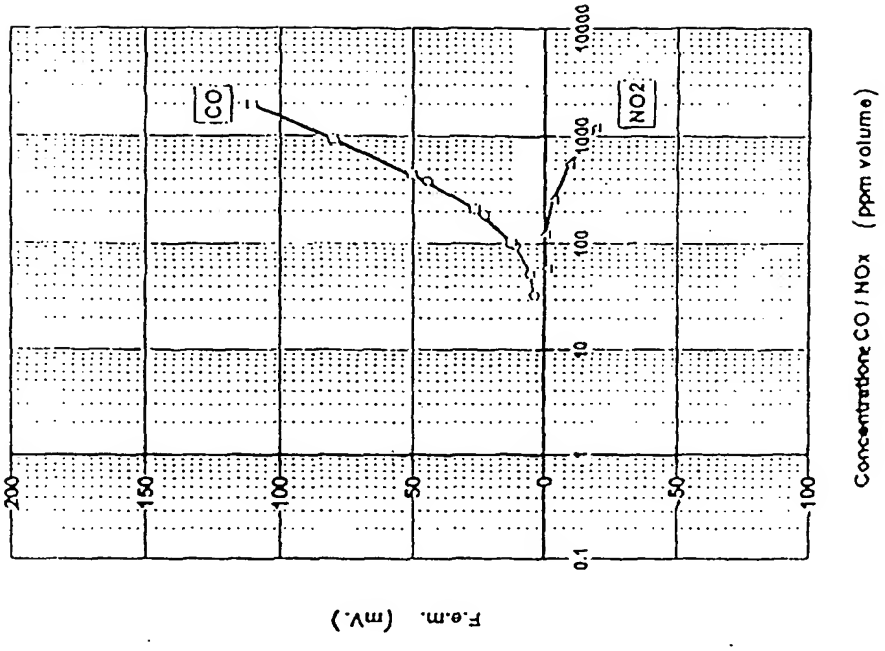
10000
50
100
F.e.m. (mV.)
Concentrations CO / NO2 (ppm volume)

FIG.6


CO
NO2
200
150
100
50
0
50
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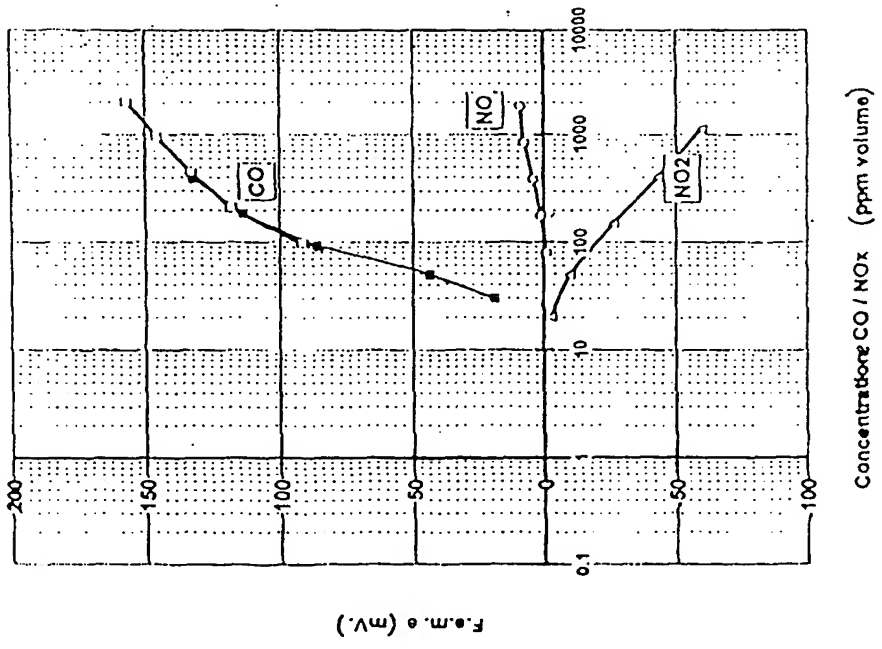
0.1
1
10
100
1000
10000
F.e.m. (mV.)
Concentrations CO / NOx (ppm volume)

FIG.5


CO
NO
NO2
200
150
100
50
0
50
100
0.1
1
10
100
1000
10000
F.e.m. e (mV.)
Concentrations CO / NOx (ppm volume)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 83 0436

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	JP 08 220059 A (TOYOTA) 30 August 1996 & US 5 656 190 A * abstract * * column 5, line 43 - line 55; figure 1 *	1	G01N27/407
A	EP 0 779 426 A (TOYOTA) 18 June 1997 * abstract * * column 3, line 10 - column 4, line 12; figure 1 *	1-7	
A	EP 0 059 636 A (THE BABCOCK&WILCOX COMPANY) 8 September 1982 * abstract * * page 3, line 12 - line 36; figure 1 *	1-7	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	9 November 1998	Kempf, G

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